

# (12) UK Patent Application (19) GB (11) 2 036 062 A

(21) Application No 7936770

(22) Date of filing 23 Oct 1979

(30) Priority data

(31) 78/43135

(32) 3 Nov 1978

(33) United Kingdom (GB)

(43) Application published

25 Jun 1980

(51) INT CL<sup>3</sup>

C09K 3/18 C23F 11/00

(52) Domestic classification

C4X 1

C1C 253 324 463 B

(56) Documents cited

GB 1110416

GB 1061756

GB 1061671

GB 976964

GB 921320

GB 921279

GB 838258

GB 578847

(58) Field of search

C1C

C4X

(71) Applicants

Smiths Industries Limited,

Cricklewood, London,

NW2 6JN

(72) Inventors

Bernard Robert Venn,

Dennis Alan Spooner,

Alton Patrick Bell,

Stephen George Rogers

Cliffe

(74) Agents

Batchellor, Kirk & Eyles

## (54) Antifreeze agents

(57) An antifreeze agent comprises a water-soluble alcohol component, such as ethylene glycol, together with the following percentages by weight (all with reference to the alcohol component) of the following substances:

about 0.02 to about 1% alkali metal or ammonium metasilicate (calculated as pentahydrate), such as sodium metasilicate:

about 0.1 to about 5% alkali metal or ammonium salt of an aromatic substituted  $\alpha,\beta$ -ethylenically

unsaturated carboxylic acid, such as sodium cinnamate;

about 0.5 to about 5% alkali metal or ammonium salt of boric acid, such as borax decahydrate;

0 to about 1% alkali metal or ammonium hydroxide, such as caustic soda;

0 to about 0.15% polycyclic heterocyclic copper corrosion inhibitor, such as benzotriazole;

0 to about 1% alkali metal or ammonium nitrite, such as sodium nitrite; and

0 to about 1% alkali metal or ammonium nitrate, such as sodium nitrate.

Certain of the chemical formula.  
appearing in the printed  
specification was submitted in  
formal form after the date of filing.

GB2 036 062 A

## SPECIFICATION

### Antifreeze agents

This invention relates to antifreeze agents.

It is common practice to mix with the cooling water of an internal combustion engine an antifreeze agent in order to depress the freezing point of the water and hence protect the engine against the effects of cold weather. It is also known to add antifreeze agents to the circulating water of central heating systems, particularly when the premises in which such systems are installed may be left vacant in winter.

Such antifreeze agents conventionally comprise an alcoholic component, such as ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, butylene glycol, methanol or a mixture of two or more of these. Since in time, acidic components may arise in the coolant, possible due to oxidation of the alcoholic component or, in the case of an engine, due to seepage of exhaust gases through a leak, it is conventional practice to incorporate in an antifreeze agent one or more corrosion inhibitors in order to protect the different metals with which the coolant may come into contact.

Engine blocks and cylinder heads, although formerly made almost exclusively from cast iron, may alternatively be made from aluminium or an aluminium alloy. For the sake of convenience it is preferred to formulate an antifreeze agent so that it is suitable for use both with cast iron and with aluminium engine heads and/or blocks. Radiators are conventionally made from copper, copper alloy, or aluminium alloy components soldered, glued or welded together. Other metallic parts with which an engine coolant may come into contact include water pumps and thermostatic valves. An antifreeze agent is therefore usually formulated with a view to providing, not only "reserve alkalinity" to provide a buffering effect against acidic substances, but also corrosion protection to the metallic materials most commonly used in engine manufacture, viz., iron, steel, cast aluminium, brass, solder and copper.

Amongst corrosion inhibitors that have previously been suggested there may be mentioned borax, sodium mercaptobenzothiazole, sodium silicate, potassium or sodium phenylaminoacetate, alkaline earth metal borates, triethanolamine, alkali metal and ammonium salts of phosphoric acid and of polycondensed phosphoric acids, benzotriazole, alkali metal arsenites, alkali metal arsenates, alkali metal molybdates, alkali metal tungstates, aliphatic, alicyclic or heterocyclic amines, sodium carbonate, sodium nitrate, sodium nitrite, and sodium benzoate. Such inhibitors are conventionally used in a combination of one to three, sometimes even more than three, compounds to prevent corrosion by antifreeze agents, but they still do not act entirely satisfactorily. For example the presence of calcium ions in the water may lead to precipitation of insoluble salts when the antifreeze agent contains phosphate, arsenate, molybdate or tungstate ions; such insoluble calcium salts may lead to blockages in the cooling system. Although polyphosphates can be added to solubilise calcium ions, they hydrolyse and lose their activity. Amines attack copper and its alloys so sodium mercaptobenzothiazole may be added to stop this. However, such antifreeze agents have unfavourable ageing characteristics and may throw down precipitates on storage.

The specifications of three typical types of approved antifreeze agent are laid down in the following British Standards: BS3150:1959, BS3151:1959 and BS3152:1959.

It is known to the expert in the art that weaknesses of individual inhibitors cannot be obviated solely by accumulating corrosion inhibitors, but that it is often the case that good properties already achieved are lost again upon the addition of further components. It is particularly difficult to develop an inhibitor combination that will give good results under varying conditions and not only with a single test and with only one kind of water. Moreover, although reserve alkalinity can be increased by increasing the amounts of such inhibitors as borates or sodium carbonate, it is considered undesirable to incorporate more than about 5% by weight of solids in the antifreeze agent lest undesirable quantities of solids should build up in a cooling system on evaporation, for example by reason of engine overheating. At least one vehicle manufacturer specifies today that, in order to qualify for approval for use in its engines, an antifreeze agent must have a reserve alkalinity of at least 15 and a solids content of not more than 5% by weight, based on the weight of the alcohol component.

According to the present invention we provide an antifreeze agent comprising a water-soluble alcohol component together with the following percentages by weight (all with reference to the alcohol component) of the following substances:

- about 0.02 to about 1% alkali metal or ammonium metasilicate (calculated as pentahydrate);
- about 0.1 to about 5% alkali metal salt or ammonium salt of an aromatic substituted  $\alpha,\beta$ -ethylenically unsaturated carboxylic acid;
- about 0.5 to about 5% alkali metal or ammonium salt of boric acid;
- 0 to about 1% alkali metal or ammonium hydroxide;
- 0 to about 0.15% polycyclic heterocyclic copper corrosion inhibitor;
- 0 to about 1% alkali metal or ammonium nitrite and
- 0 to about 1% alkali metal or ammonium nitrate.

Throughout this specification, except where otherwise specified, all percentages are by weight.

Preferably the alkali metal in the salts is sodium since sodium compounds are generally cheaper





benzotriazole, then it is preferably present in an amount of from about 0.05 to about 0.15% based on the weight of the alcohol component.

If a nitrite is added, e.g. sodium or potassium nitrite, it is preferred to utilise from about 0.05 to about 0.3% based on the weight of the alcohol component.

5 The preferred nitrates are sodium nitrate and potassium nitrate. 5

The antifreeze agent of the present invention can be prepared in any convenient manner, preferably by admixing with the alcohol component the specified additives in the amounts indicated. Preferably the antifreeze agent comprises at least about 85%, and usually at least about 95% up to about 99.38% of the alcohol component; it may further comprise a small amount, for example, less than 10 about 5% by weight, of water, based upon the weight of the alcohol component. Such small amounts of 10 water may assist in solubilising some of the additives.

As examples of suitable antifoam agents there may be mentioned silicone oils, polyglycols (e.g., polyoxypropylene glycols of molecular weight about 950 to 1950 which have been reacted with ethylene oxide to give copolymers containing up to about 30% by weight of ethylene oxide residues), 15 mineral oils, *iso*-octanol, C<sub>6</sub> to C<sub>12</sub> alcohols (e.g., C<sub>7</sub> to C<sub>9</sub> Oxo alcohols), organic phosphates, alkyl 15 lactates and castor oil soaps. Such antifoam agents may be added, for example, in amounts of from about 0.0005 to about 0.05%, based on the weight of the alcohol component.

The amounts of boric acid salt and of alkali hydroxide or ammonium hydroxide are preferably so chosen that the pH of a 25 vol.% solution in distilled water of the antifreeze agent is not greater than 20 about 10.0 and preferably lies in the range of from about 7.5 to about 8.5. Moreover the agent is 20 preferably so formulated that its solids content is less than about 5% by weight, based on the weight of the alcohol component and its reserve alkalinity is at least about 15.

The antifreeze agents of the present invention are suitable for use as, for example, about 10 to about 60 vol.% aqueous solutions in the cooling systems of internal combustion engines. Usually they 25 will be utilised as about 20 to about 33 vol.% aqueous solutions for this purpose. They can also be used 25 in domestic and other circulating water central heating systems as well as in other equipment.

The invention is further illustrated in the following Examples. In these Examples the results were obtained using the glassware test apparatus described in BS 5117:1974 "Methods of Test for Corrosion Inhibition Performance of Antifreeze Solutions" published by British Standards Institution, 2 30 Park Street, London W1A 2BS. 30

#### EXAMPLE 1.

An antifreeze agent was prepared by admixing with 100 parts by weight of ethylene glycol (ethanediol) the following constituents:

	<u>Constituent</u>	<u>Parts by weight</u>	
35	Borax decahydrate	2.5	35
	Sodium nitrite	0.15	
	Benzotriazole	0.15	
	Cinnamic acid	1.32	
	Caustic Soda	0.40	
40	Disodium metasilicate pentahydrate	0.20	40

Upon testing in the glassware test (BS 5117:1974) the mean weight loss per specimen at 20 vol.%, 25 vol.%, and 33 $\frac{1}{3}$  vol.% (diluted with standard test water) was as shown in Table 1. After testing, the specimens were chemically cleaned, prior to weighing, in order to remove adhered corrosion 45 products. 45

TABLE 1

	Copper	Solder	Brass	Mild steel	Cast iron	Cast aluminium
20 vol %	1.0mg	1.5mg	1.5mg	1.0mg	1.0mg	2.5mg
25 vol %	1.0mg	1.0mg	0.0mg	1.0mg	1.0mg	1.5mg
33½ vol %	2.0mg	0.5mg	0.0mg	2.0mg	1.5mg	2.5mg

The antifreeze agent of this Example has a solids content of 4.72% and showed a "reserve alkalinity" of over 15. For comparison an antifreeze composition of the type described in United Kingdom Specification No. 945638 was made up having a solids content of 4%; this had the following composition:

Constituent	Parts by weight
Ethylene glycol	100
Borax decahydrate	1
Potassium nitrate	0.3
10 Sodium nitrite	0.35
Sodium benzoate	2.26
Sodium metasilicate	0.03
Benzotriazole	0.07

The "reserve alkalinity" of this composition was 9.5. "Reserve alkalinity" is defined (according to BS 5117:1974) as the number of millilitres of 0.1 N hydrochloric acid required for titration of 10 ml of concentrated antifreeze, or its equivalent, to a pH value of 5.5. Usually a 10 ml sample of antifreeze is diluted to 100 ml with distilled water prior to titration.

#### EXAMPLE 2.

Three antifreeze agents (hereafter called, A, B and C), were prepared each by adding to 100 parts by weight of ethylene glycol the following ingredients:

Constituent	Parts by weight
Borax decahydrate	2.5
Sodium nitrite	0.15
Benzotriazole	0.15
25 Cinnamic acid	1.32
Disodium metasilicate pentahydrate	0.1
Caustic soda	x*

(\*See Table 2 below)

These agents gave rise to the results listed in Table 2 upon testing according to the glassware test (BS 5117:1974) at 33½ vol.% (i.e. 33½ vols. agent mixed with 66½ vols. standard test water).



TABLE 2

Agent	x	Weight loss per specimen in mg.						pH
		Copper	Solder	Brass	Mild steel	Cast iron	Cast aluminium	
A	0.35	0	2	1	+2	1	2	7.8
B	0.40	1	0	1	0	0	1	7.85
C	0.50	1	2	0	+2	1	0	8.0

All specimens were chemically cleaned to remove adherent corrosion products prior to weighing. A plus sign (+) in front of a reading indicates a weight gain. Each of agents A to C had a "reserve alkalinity" of more than 15 despite having solids contents (based on ethylene glycol) of only 4.57%, 4.62% and 4.67% respectively.

5

## EXAMPLE 3.

Two antifreeze agents (hereafter called D and E) were made by adding to 100 parts by weight of ethylene glycol the following ingredients:—

	Constituent	Parts by weight	
10	Borax decahydrate	2.5	10
	Sodium nitrite	0.15	
	Benzotriazole	0.15	
	Cinnamic Acid	1.32	
15	Disodium metasilicate pentahydrate	y**	15
	(**See Table 3 below)		

These 3 antifreeze agents were subjected to the glassware test of BS 5117:1974 and gave the results listed in Table 3 at 15 vol.% (i.e. 15 vols. of agent diluted with 85 vols. standard test water).

TABLE 3

Agent	y	Weight loss in mg per specimen					
		Copper	Solder	Brass	Mild steel	Cast iron	Cast aluminium
D	0.32	0	2	1	+1	0	0
E	0.20	1	2	2	0	2	13

Both agents D and E had a "reserve alkalinity" of more than 15, despite a solids content (based on the weight of ethylene glycol) of only 4.44% and 4.32% respectively.

## EXAMPLE 4.

An antifreeze agent is prepared according to the directions given in Example 1 except that the 0.15 parts by weight of benzotriazole is replaced by 0.15 parts by weight of tolyltriazole. Similarly good results are obtained.

25



